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14. ABSTRACT The lipid fraction of herbor sediment organic matter is found to be a significant control on the binding of PAHs. In the absence of lipids, binding is more nonlinear and the binding domain can be characterized as an "immobile" chemical environment from the PAH's perspective. Additional experiments with authentic polymers raise questions about the applicability of dual-mode sorption model to natural organic matter.					
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Contract Information

Contract Number	N00014-99-1-0587
Title of Research	Nature and Formation of PAH and PCB Bound-Residues in the Humin Fraction of Harbor Sediments
Principal Investigator	James A. Rice
Organization	South Dakota State University

Technical Section

Technical Objectives

The humin fraction of humic substances is the predominant organic material in most sediments; humin organic-carbon typically represents substantially more than 50% of the total organic-carbon present. A significant fraction (typically >50%) of most anthropogenic hydrophobic organic compounds (e.g., polynuclear aromatic hydrocarbons (PAHs)) introduced into the sediment environment binds rapidly, and in many cases, irreversibly, to it. Yet very little is known about the actual nature of organic contaminants bound, or the nature of their interaction with humin.

The goal of this research is to develop an understanding of contaminant binding to the humin fraction of sediment organic matter. The objectives of this study can be placed into two groups; to study contaminant-humin binding mechanisms and to develop a model to describe the binding phenomena. The specific objectives of this project were:

Contaminant-Humin Binding Mechanisms

1. determine whether polynuclear aromatic hydrocarbons and polychlorinated biphenyls bound to harbor sediment humin are more likely to be associated with the insoluble residue, the lipid (bitumen and/or bound lipid) or the bound-humic acid components of humin. It is proposed that the greatest affinity for PAH bound-residues will be displayed by the bound-lipid fraction.
2. begin to identify the nature of the bound contaminants. Determine whether it is the parent contaminant itself, or its degradation or alteration product which is bound to humin.
3. describe the nature of the contaminant binding environment in humin. It is proposed that PAHs are first associated with the more "fluid-like" organic phases (ie, the lipid fractions) and with time, enter a more rigid environment (ie, are bound to the bound-humic acid component of humin).

Modeling the Binding Phenomena

4. determine the role of bitumen and bound lipids in the binding of contaminants to humin. Specifically, it is proposed that contaminants are first partitioned into the bitumen and/or bound-lipid components of humin before being irreversibly bound, and that the removal of bitumen from a humin sample will decrease its affinity for these compounds.
5. develop a conceptual model to describe contaminant binding to harbor sediment humin. It is proposed that the process of bound residue formation can be best described by a distributed reactivity model.

By advancing our understanding of contaminant binding to humin, this study has provided information that can be used to predict their fate in natural sediment systems (Objectives 1, 2, and 3). An understanding of the factors that control the binding and desorption of contaminants to humin provides information that can be used to better model their transport in a natural system (Objectives 3, 4 and 5) and ultimately facilitate the remediation of contaminated sediments.

Technical Approach

In this study ^{14}C -, ^{13}C -, and ^{19}F -labeled PAHs (naphthalene, fluorene, and phenanthrene) were incubated with contaminated and uncontaminated harbor sediments in separate microcosm experiments. Using scintillation counting, differential scanning calorimetry, ultrafiltration, solution- and solid-state NMR, and mass spectrometry, the qualitative and quantitative nature of contaminant binding to humin was examined to identify the substances being bound, provide a description of the binding environment, and model the binding phenomenon. This study provides information from which an understanding of the factors that control the binding and desorption of contaminants to sediment organic matter can be developed. Ultimately, the results of this study may lead to the selection of appropriate remediation strategies for a particular site and improved risk assessment.

Findings

1. Influence of Lipids on PAH Sorption to Harbor Sediments

The sorption isotherms of naphthalene, fluorene, and phenanthrene for several different chemically treated fractions of sediment obtained from the harbor at San Diego, CA are presented. Sorption isotherms to the native sediment are linear for naphthalene and fluorene but nonlinear for phenanthrene (Figure 1). Chemical treatments to sequentially remove the organic matter from the sediment show that the isotherm sorption character becomes increasingly nonlinear with removal of natural lipids. Removal of lipids also increases the capacity of the sorbent for the each PAH. The nonlinear sorptive character of the lipid-extracted sediment can be described by site specific sorption. Lipids naturally present in the sediment that compete for PAH sorption sites normally occupy these sites.

This work has been submitted for publication².

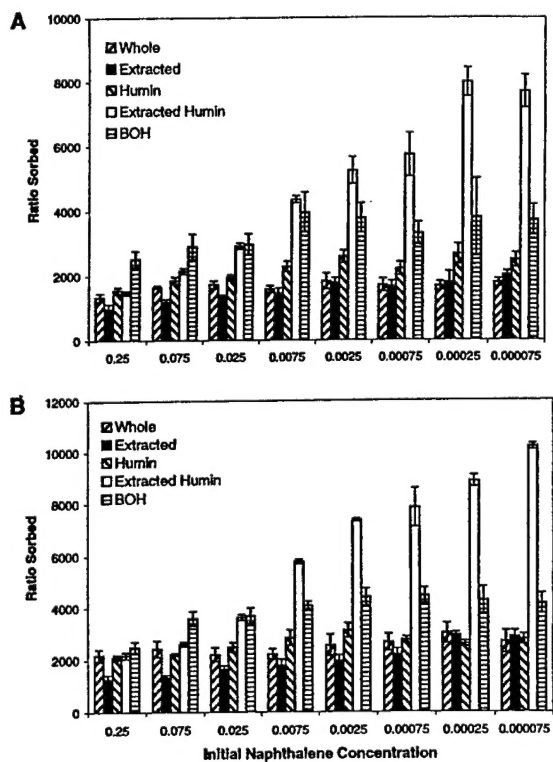
2. Role of Lipids in PAH Binding to Sediment

The importance of the role of the lipid fraction of natural organic matter in the sorption of polycyclic aromatic hydrocarbons was assessed by several different procedures. First, phenanthrene was sorbed on marine sediments as well as their humin and humic acid fractions before and after lipid extraction. Before lipid extraction, the sorption shows partitioning characteristics. However, the extraction of lipids from sediment and humin drastically increases their sorption affinity for phenanthrene at low sorbate concentrations resulting in increased isotherm nonlinearity. This effect is less pronounced for humic acids. This result provides evidence that lipids, despite their low relative abundance in the natural samples studied, can compete with phenanthrene for specific high affinity sorption sites (e.g., matrix pores and adsorption sites) or may act like plasticizers for rigid domains limiting adsorption. Second, re-addition of lipids to the sediment restores the sorption isotherm linearity observed in the native material supporting the absence of extraction artifacts. However, if an excess of lipids are added during this process, lipids can promote phenanthrene sorption in a manner having partitioning characteristics. These results are in agreement with dual-mode hole-filling sorption models involving sorbate pore and/or matrix diffusion. Finally, solid-state ^{19}F NMR using F-labeled lipid sorbed onto the geosorbents shows that lipids have a varying mobility in different domains which may interact with phenanthrene (Figure 2).

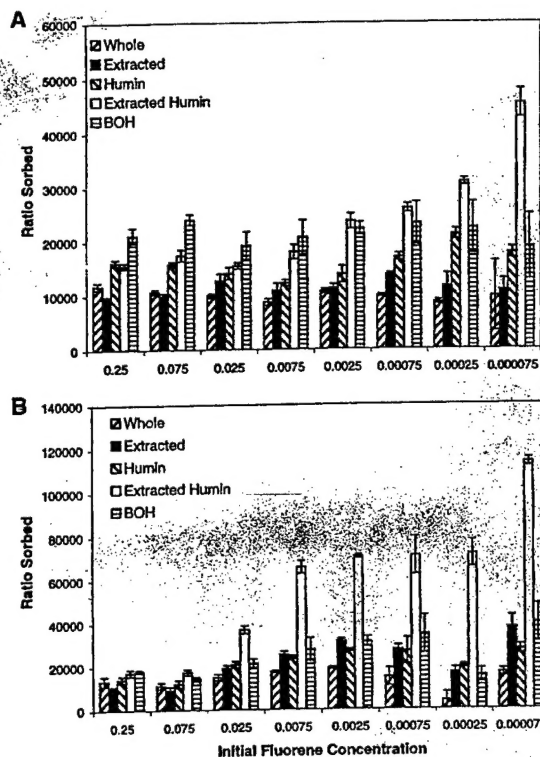
This study has been submitted for publication³⁻⁴.

Figure 1. Sorption isotherm of naphthalene, fluorene, and phenanthrene to sediment fractions after (A) 1 and (B) 7 days. Ratio sorbed - $\mu\text{g/g}$ organic carbon in solid phase to $\mu\text{g/mL}$ solution phase. Initial concentration is aqueous phase in multiples of the water solubility of the PAH. Whole sediment (whole), solvent-extracted sediment (extracted), sediment humin (humin), solvent-extracted humin (extracted humin), extracted humin treated with Br_2 to remove remaining organic matter (BOH). Organic matter was selectively removed from the samples as follows: Whole, Extracted (removal of lipids), Humin (removal of humic and fulvic acids), Extracted Humin (removal of bound lipids), BOH (removal of essentially all remaining organic matter).

Naphthalene



Fluorene



Phenanthrene

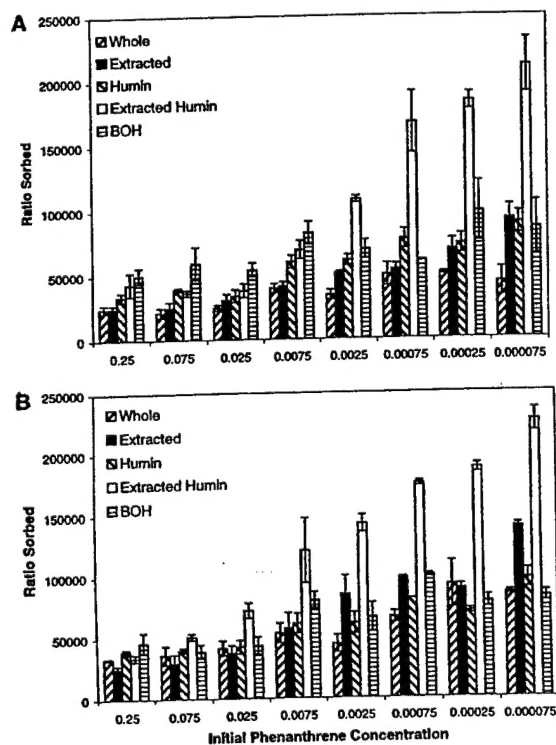
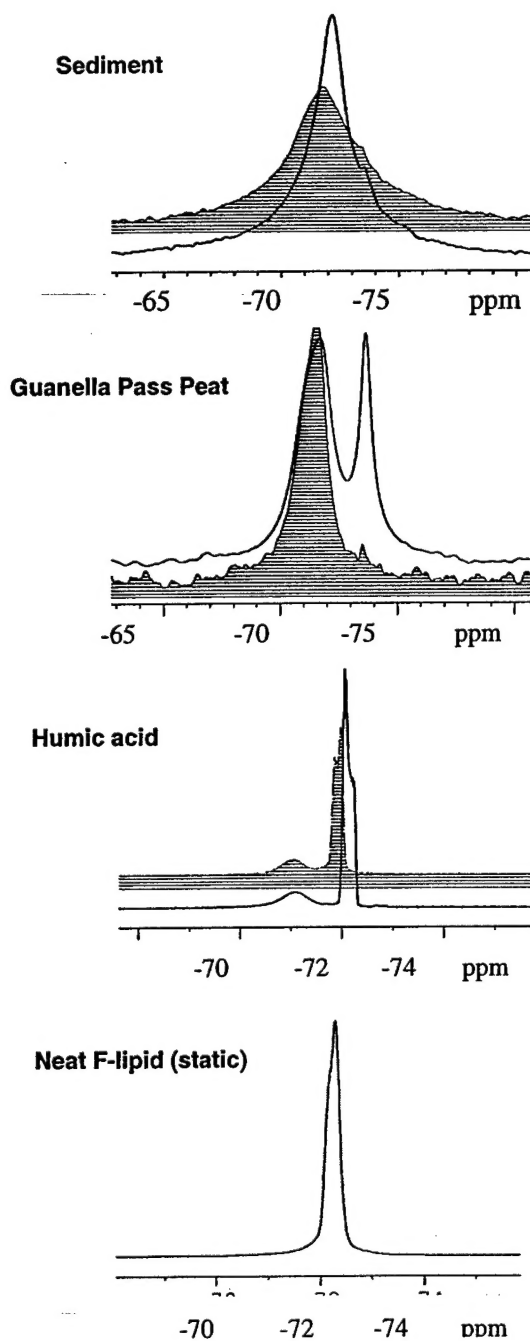


Figure 2. Solid-state ^{19}F NMR spectra of 2,2,2-trifluoroethyl laurate neat (static) and sorbed on geosorbents (MAS) after 7 days in solution with (shaded spectra) and without phenanthrene.



3. PAH Sorption to Suspended Sediment and Particulate Organic Matter

The sorption of phenanthrene and fluoranthene on suspended estuarine particulate matter (SPM), including humic acids, was studied in batch experiments under varying conditions of temperature, salinity, and dissolved organic matter (DOM) concentrations. A decrease in water temperature and an increase in salinity, such as that encountered in estuaries during the transition from river to seawater, increased the fraction of these contaminants sorbed to the particles (Figure 3). Together, these changes in temperature and salinity increased the sorption to the SPM by 40% to 64%. Although the same average increase was determined for particulate humic acids, a different effect of sorbate concentrations was observed. The extent of both the effect of temperature and salinity variations can be chiefly attributed to changes in the contaminant water solubility. Along with calculated isotherm parameters, sorption enthalpies and entropies, these results support a process that can primarily be described as partitioning. However, slightly

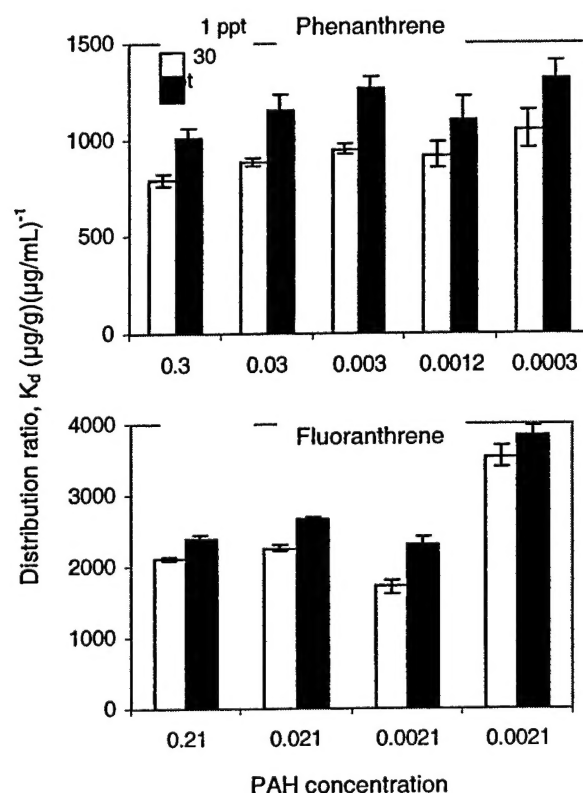


Figure 3. Distribution ratio for PAH sorption on SPM 20 m at two different water salinities (in ppt) as a function of the initial solution PAH concentration at 20°C. Concentrations are expressed in multiples of the PAH water solubility.

nonlinear isotherms and the more exothermic sorption at low sorbate concentrations seem to indicate the presence of relatively few site-specific interactions. The effect of dissolved humic substances upon sorption onto SPM was very small for fluoranthrene, with a higher affinity for humic acid compared to fulvic acid, and not detected for phenanthrene. The impacts of the three parameters studied upon sorption and sediment trapping within estuaries may be less important than those caused by changes in the nature or in the concentration of the geosorbent.

This work is currently being prepared for publication⁵.

4. Effect of Organic Matter Molecular Size on Contaminant Sorption

Humic acid was fractionated into eight different molecular size components using tangential flow ultrafiltration. Solid-state CPMAS ^{13}C NMR demonstrated that fractions larger than 100,000 Daltons were primarily aliphatic in character while fractions smaller than 30,000 Daltons were predominantly aromatic in character. Solid-state ^{19}F NMR examination of the sorptive uptake of hexafluorobenzene (HFB) by humic acid and each of its fractions gave spectroscopic evidence for the existence of at least three sorption sites in the smaller molecular size fractions while two predominant sorption sites could be established in the larger molecular size fractions (Figure 4). Sorbed HFB displayed higher mobility in the smaller, more aromatic fractions while HFB in the larger, more aliphatic fractions displayed lower mobility. The relative mobility of HFB in each sorption domain suggests that the rigid domain may be composed of aliphatic carbon rather than aromatic carbon moieties. This domain may be the result of rigid, glassy regions composed of aliphatic molecules or side chains. Natural lipids present in HA may act as a "plasticizer" for glassy regions that decrease the rigid sorption character of those regions.

This study has been published⁶.

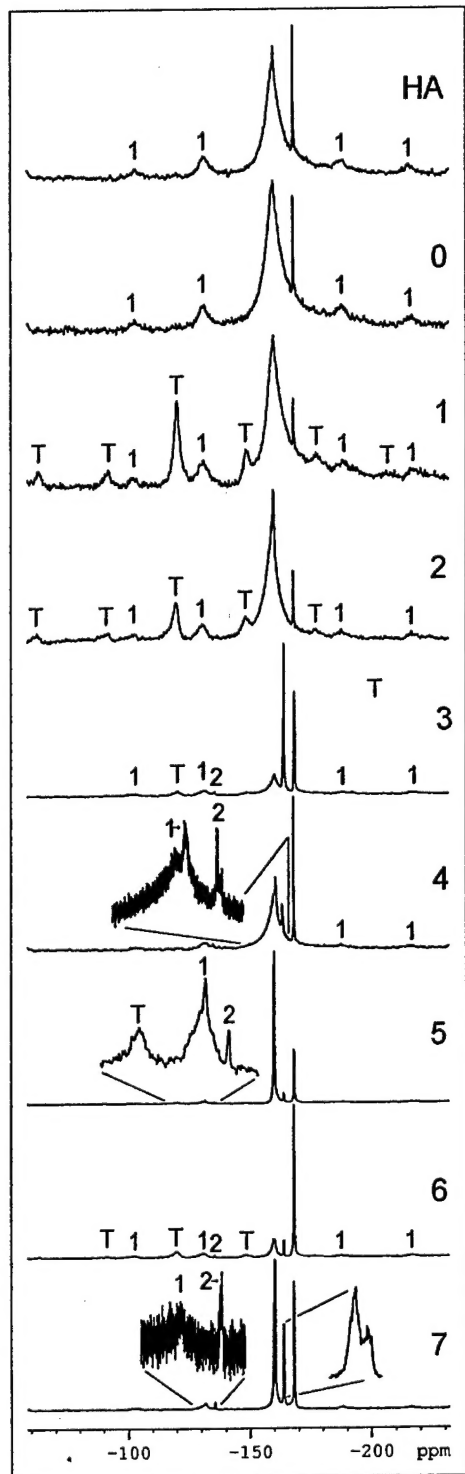


Figure 4. ^{19}F NMR spectra for sorption of hexafluorobenzene to humic acid and ultrafiltration fractions. 1 denotes sidebands from -160 ppm resonance, 2 denotes sidebands from -164 ppm resonance, and T denotes sidebands from PTFE contamination (PTFE isotropic peak at -120 ppm). Molecular sizes decrease from fraction 0 ($\geq 100,000$ Daltons) through fraction 7 (≤ 1000 daltons).

5. Temperature Effects on the Sorption of PAHs to Sediments

There are few studies to probe the temperature dependence of sorption of hydrophobic organic contaminants to natural sorbents in saturated aqueous systems. The temperature dependence should be examined even beyond environmental limits because it can offer critical

Table 1. Thermodynamic parameters calculated from sorption data for (a) pyrene, (b) fluorene, and (c) phenanthrene. SD – San Diego Bay harbor sediment, GP - Guanella Pass peat, and the other 3 samples are soils. na - not available.

sample (a)	ΔH (kJ/mol)		ΔS (J/mol K)	
	whole	extracted	whole	extracted
SD	-21.7 ± 7.0	-20.5 ± 8.0	-18.1 ± 5.8	-7.4 ± 2.9
AS	-6.8 ± 4.0	-18.7 ± 9.0	47.5 ± 28.0	11.1 ± 4.9
HS	-16.0 ± 11.0	-22.5 ± 11.0	16.34 ± 11.0	-2.5 ± 2.5
PS	-10.7 ± 6.0	$- \pm$	36.3 ± 18.0	$- \pm$
GP	-20.2 ± 1.3	-31.1 ± 3.6	9.9 ± 1.6	-26.5 ± 3.6

Sample (b)	ΔH (kJ/mol)		ΔS (J/mol K)	
	whole	extracted	whole	extracted
SD	-9.3 ± 2.4	-13.2 ± 7.0	9.4 ± 2.4	-0.4 ± 1.3
AS	-12.0 ± 3.0	-19.5 ± 0.9	16.2 ± 4.0	-3.6 ± 0.2
HS	-10.3 ± 3.2	-20.5 ± 1.3	20.6 ± 6.4	-7.7 ± 0.5
PS	-14.4 ± 4.5	-20.7 ± 3.6	8.61 ± 2.9	-6.8 ± 1.2
GP	-24.9 ± 1.1	-33.6 ± 1.9	-10.3 ± 2.5	-38.3 ± 4.5

Sample (c)	ΔH (kJ/mol)		ΔS (J/mol K)	
	whole	extracted	whole	extracted
SD	na	na	na	na
AS	-10.1 ± 3.0	-13.3 ± 2.6	11.4 ± 3.4	5.5 ± 1.0
HS	-9.0 ± 2.4	-17.7 ± 1.7	13.9 ± 3.6	-7.1 ± 0.7
PS	-6.4 ± 2.0	-12.6 ± 1.2	24.2 ± 7.5	8.6 ± 0.8
GP	-20.7 ± 3.4	-27.9 ± 3.4	-6.0 ± 0.9	-26.5 ± 2

information about the sorption mechanism.

Laboratory sorption experiments were conducted with pyrene, phenanthrene, and fluorene and five different soils and sediments that exhibited organic carbon contents between 1 and 26% at four different temperatures using a batch technique. The samples were studied with and without extraction to remove lipids. The equilibrium PAH distribution coefficients at 10°C, 20°C, 30°C, and 40°C were determined. For all PAHs and all sorbents, temperature affected the distribution coefficients. The van't Hoff equation was used to calculate the enthalpy of sorption for those systems where the enthalpy was independent of temperature over the temperature range studied. The free energy and entropy of sorption were calculated from standard thermodynamic equations. The calculated ΔH values suggest a weak type of bonding (between 6 and 14 kJ/mol for fluorene, between 10 and 18 kJ/mol for phenanthrene, and between 9 and 20 kJ/mol for pyrene). However, the values for extracted samples were twice the values of whole samples for fluorene, one and a half times that for phenanthrene, and almost identical for pyrene. The free energy was negative for all samples, as would be expected for spontaneous reactions. However, the values were more negative for pyrene than for phenanthrene and fluorene. The entropy values were more positive for pyrene than for the other contaminants. It appears that pyrene sorption is more entropy driven than of either phenanthrene or fluorene. The sorbent containing 26% organic carbon displayed different sorption behavior than any of the other samples. Both the whole and extracted samples exhibited a sorption discontinuity in the 30°C -40°C range which was more pronounced for fluorene than for phenanthrene, and was almost nonexistent for pyrene. Moreover, the whole sample showed a glass transition at 37°C that was not observed in the extracted sample. A manuscript from this work has been submitted for publication⁷ and a second is currently being prepared for publication¹¹.

The last phase of this study is examining the differences in binding environment mobility that is suggested by the glass transition at 37°C using variable-temperature, quantitative ¹³C solid-state NMR. These experiments are just beginning and will be presented in the final dissertation acknowledging support from this award.

6. Formation of bound residues by naphthalene and cis-naphthalene-1,2-dihydrodiol

The formation of bound residues by naphthalene and its metabolite, cis-naphthalene-1,2-dihydrodiol, in the San Diego Bay harbor sediment (1% OC), a silty loam soil (2.9% OC) and a peat (26% OC) was examined. The experiments were carried out under both sterile and nonsterile conditions. The samples containing bound contaminant were hydrolyzed at an alkaline pH and fractionated using 3000 and 500 Dalton molecular weight cutoff ultrafiltration membranes in series. The results showed that bound residue formation is low for naphthalene and between 5 and 20 times higher for the metabolite (Figures 5 and 6). The amount of bound residues released by hydrolysis after three days was higher for the metabolite than for the parent compound. The molecular weight distribution of bound radioactivity after hydrolysis showed binding to the high molecular weight components of the sediment organic matter and to the low molecular weight components for soil and peat organic matter when incubated with its metabolite cis-naphthalene-1,2-dihydrodiol (Table 2). This suggests that it is the metabolite rather than the parent PAH which is being bound.

This work has been submitted for publication⁸.

Figure 5. Mass of naphthalene bound residues normalized to the organic carbon content for each sample.

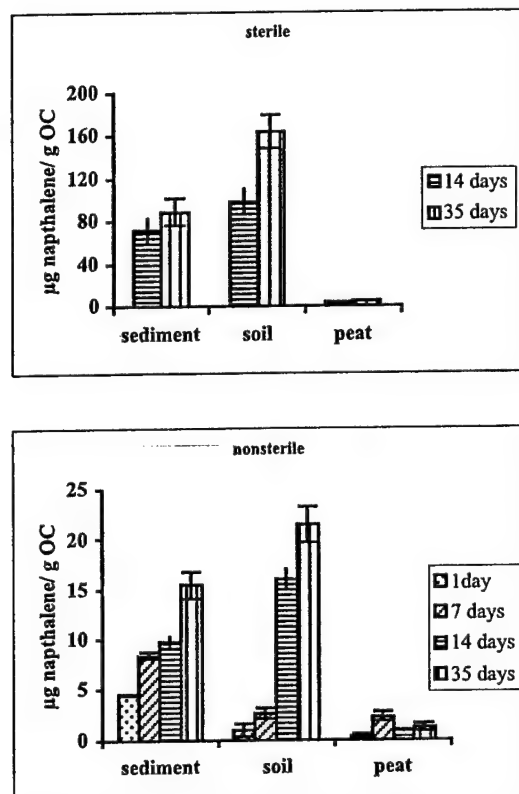


Figure 6. Mass of cis-naphthalene-1,2-dihydrodiol bound residues normalized to the organic carbon content for each sample.

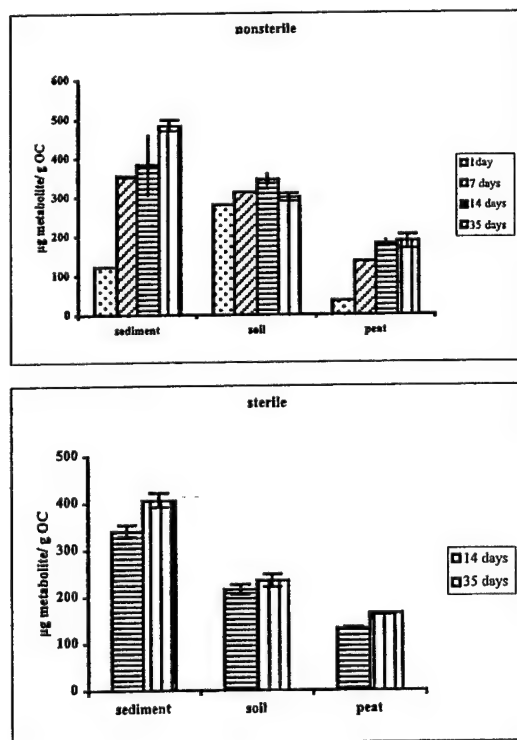


Table 2. Distribution of ^{14}C with molecular weight after alkaline hydrolysis of extracted samples that had been incubated for 35 days.

<i>Sample</i>	<i>Conditions</i>	% Bound Residue hydrolyzed	>3000	500-3000	<500
Sediment /	nonsterile	82 ± 12	43 ± 3	0.3 ± 0.04	57 ± 3
diol	sterile	78 ± 4	39 ± 1	7.6 ± 5.6	53 ± 5
Soil / diol	nonsterile	45 ± 1.7	15 ± 3	9 ± 13	75 ± 12
	sterile	57 ± 4	2 ± 7	27 ± 21	71 ± 19
Peat / diol	nonsterile	28 ± 1.6	4 ± 0.2	4 ± 18	89 ± 18
	sterile	27 ± 1	28 ± 9	2 ± 12	69.2 ± 8
Sediment /	nonsterile	30 ± 1	na	na	na
naphthalene	sterile	50 ± 6	46 ± 3	35 ± 5	23 ± 10
Soil /	nonsterile	36 ± 3	49 ± 3	14 ± 6	37 ± 2
naphthalene	sterile	36 ± 2	45 ± 3	47 ± 9	6 ± 3
Peat /	nonsterile	2 ± 7	na	na	na
naphthalene	sterile	4 ± 0.8	na	na	na

7. Role of lipids in PAH sorption/desorption hysteresis

The chemical composition of natural organic matter plays a major role in regulating its capacity to retain hydrophobic organic compounds. Naphthalene and phenanthrene were used to study the correlations between sorption/desorption isotherm nonlinearity and compositional data from soil and peat organic matter (with or without lipids) obtained from quantitative ^{13}C solid-state NMR spectroscopy. The sorption experiments were conducted using a batch equilibration method. Desorption experiments were carried out immediately following the sorption experiments by 3 successive decant-refill cycles. Hysteresis was observed in all samples. Nonlinear sorption behavior was increased by removal of lipids from the organic matrix. Desorption increased with increasing of solution concentrations of naphthalene and phenanthrene and then decreased at the highest concentration point with or without the presence of lipids. The hysteresis index, obtained from the ratio of the Freundlich exponents (N values) for desorption and sorption, was lower in the lipid-extracted organic fractions than in those of same samples without lipid extraction. The relationship between the extent of hysteresis and the characteristics of quantitative solid-state ^{13}C DPMAS NMR spectra indicated that altering natural organic

matter composition through lipid extraction not only increased the proportion of the aromatic-C content, but also increased sorption/desorption hysteresis.

This work has been submitted for publication⁹.

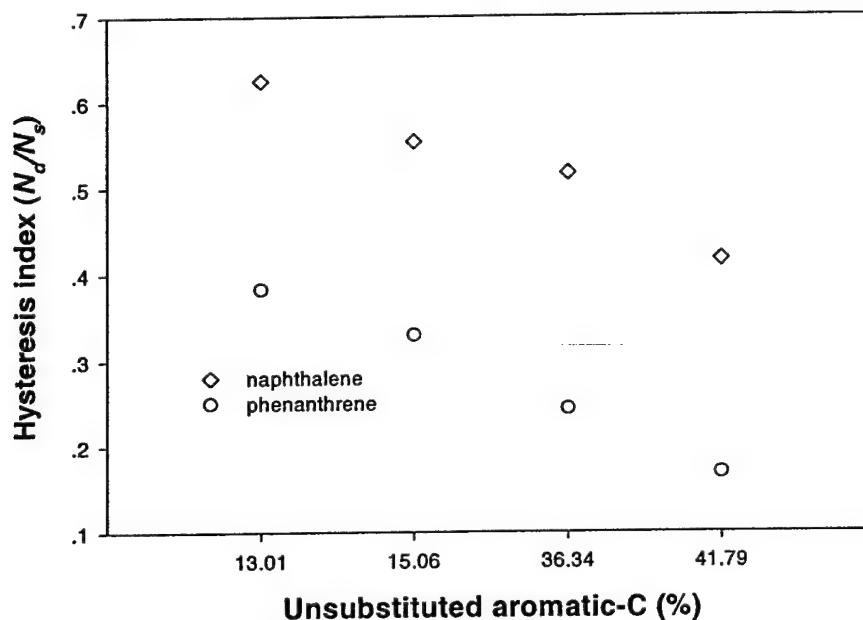


Figure 7. Correlation of hysteresis index with unsubstituted aromatic-carbon from quantitative solid-state ^{13}C DPMAS NMR spectra.

8. Assessing glassy polymers as model NOM systems in PAH binding studies

Natural organic matter (NOM) has the ability to sorb hydrophobic organic chemicals that have been introduced into the environment. Contaminant-NOM interaction models have been proposed that predict that NOM contains a rigid, glassy polymer-like, sorption domain that is responsible for binding contaminants strongly. The contention of the series of interaction models is that the sorption character of NOM is like that of the authentic polymers. The objective of this study was to assess the sorption of PAHs to authentic glassy and rubbery polymers as a model of PAH sorption to the glassy domain of NOM. Sorption isotherms (eg, Figure 8) were developed by sorbing ^{14}C -labeled PAHs from aqueous solution to glassy polymers possessing a range of glass transition temperatures (i.e., 15° to 175°C). The exponent N in the Freundlich equation, $S=K_F C^N$, was used to quantify the degree of nonlinearity. PAH sorption to authentic glassy polymers can exhibit both partition- and nonpartition-like sorption behavior regardless of the phase transition. Nonlinearity may be observed with glassy polymers given extended incubations times (i.e., > 14 days); however, this may not be applicable to NOM, since we have previously shown whole mineral and organic soils to exhibit nonlinearity within 1 to 7 days incubation. Equating the sorption character of NOM to glassy and rubbery polymers is questionable given the NOM's heterogeneity and polyfunctionality.

This work is currently being prepared for publication¹⁰.

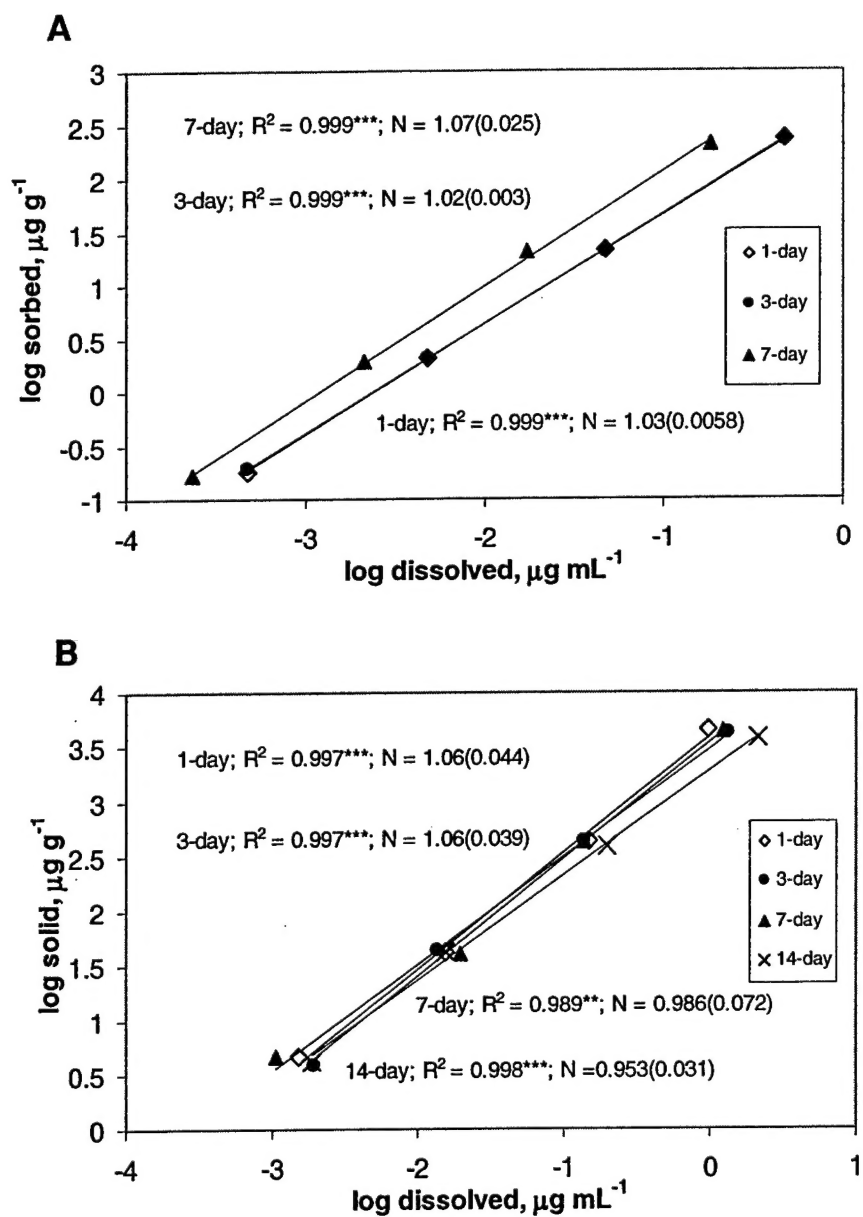


Figure 8. Freundlich model fits of (A) fluorene sorption at 1, 3, and 7 day incubation and (B) naphthalene sorption at 1, 3, 7, and 14 day incubation on PBMA at 25°C.

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2. Kohl, S. D.; Rice, J. A., 2003, Sorption of polycyclic aromatic hydrocarbons to marine sediments. Influence of natural organic matter on sorption isotherms, Chemosphere, IN REVIEW.
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9. Ding, G.*; Rice, J. A., Effect of lipids on sorption/desorption hysteresis of hydrophobic organic compounds in natural organic matter, Environmental Science & Technology, IN PREPARATION.
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13. Ding, G.*; Rice, J. A., Correlation of soil organic matter carbon-type distribution to the sorption and desorption of hydrophobic organic compounds, SA-CSSA-SSSA Ann. Mtg., November, 2003, Denver, CO, TO BE PRESENTED.

Dissertation/Theses Acknowledging Support from this Award

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3. Tremblay, L., 2003, Geochemical and Analytical Contributions in the Study of Humic Substances from the St. Lawrence Marine System, Université du Québec à Rimouski (Canada), PhD, Chemical Oceanography, 351 pp.
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Students Supported by this Award

Postdoctoral research associates: 3

Graduate students: PhD – 3; MS – 1

Undergraduate students: 3